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## REASONS FOR THE DIFFERENT EFFECTS OF CALCAREOUS CLAYS ON STRENGTH PROPERTIES OF CERAMICS

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It is demonstrated that the strength properties of ceramic products molded from poorly sintering polymimetal low-melting argillaceous materials and calcareous clays improve due to an increasing content of the total montmorillonite component in the batch; due to organogenic calcite in calcareous clays, which in firing facilitates the formation of a local reducing medium that affects the transformation of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  and facilitates earlier sintering of clay; and due to a gypsum impurity contained in calcareous clays, which is an intense flux.

Calcareous clays are promising materials for producing construction ceramics. Bricks bases on such clay have a strength grade of 100–200, frost resistance grade F15–F25, and color ranging from pink to light yellow. Light-colored facing tiles for interior decoration have acceptable properties. The light color of the ceramics is due to the presence of a substantial quantity of carbonates in clay. This occurs due to the formation in firing of iron-bearing minerals capable of binding iron oxides: bicalcium ferrite  $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$  and melilite, which is a solid solution of helenite  $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  and ferric okermanite  $2\text{CaO} \cdot \text{FeO} \cdot 2\text{SiO}_2$  [1].

Using x-ray phase analysis, it was found that calcareous clay material from the Maksimkovskoe deposit (Republic of Tatarstan) in firing produces such minerals as wollastonite ( $\text{SiO}_2 + \text{CaO} \rightarrow \text{CaO} \cdot \text{SiO}_2$ ) and helenite ( $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{CaO} \rightarrow \text{Ca}_2\text{Al}[(\text{Si}, \text{Al})_2\text{O}_7]$ ). When siliceous carbonate-bearing rock (40%; here and elsewhere wt.%) is introduced into a polymimetal argillaceous material, the ceramic also exhibits newly formed phases: wollastonite and to a smaller extent cristobalite. In this case the strength properties of ceramics increase or remain unchanged with a simultaneous decrease in the average density. Consequently, the formation of wollastonite is one of the reasons for the strength increase.

The studies indicate that adding a lime-containing clay to low-melting polymimetal clay mixtures has an ambiguous effect on the physicomechanical properties of ceramics. When the additive is introduced into a well-sintering argillaceous material, the strength properties of ceramics in fact do not change. When the additive is added to a poorly sintering material, the strength properties clearly improve, the bending property growing to a higher extent (for instance, with

30 wt.% lime clay in the argillaceous material from the Sakharovskoe deposit, the compressive strength of ceramics under certain conditions grows 1.25 times and the bending strength grows 1.5 times). The reason for such behavior of calcareous clay had to be investigated. Its main difference from a polymimetal low-melting clay is a substantial content (10–55%, on the average 30%) of organogenic calcite. Its also contains argillaceous minerals (35–80%), quartz (1–5%), impurities of gypsum, pyrite, glauconite, and iron hydroxides. Table 1 lists the content of the main oxides in the considered clays and their mixtures. Nizhne-Suksinskoe clay has good sinterability, whereas Sakharovskoe clay is a poorly sintering material. All analytical and technological studies were carried out at the Analytical Certifying Test Center of the Central Research Institute of Geology of Nonmetallic Minerals (TsNIIgeolnerud).

To reveal the reasons for the different effect of lime-containing clay on mechanical parameters of ceramics, one should primarily consider processes occurring under firing. The physicochemical processes and structural modifications occurring in ceramic mixtures in their preparation and primarily in heat treatment are reflected in the phase composition, structure, and properties of resulting materials. The evolution of high-temperature phases to a great extent depends on the structure of argillaceous minerals and the presence of small quantities of certain components.

Calcium and magnesium carbonates in a highly dispersed state are intense fluxes due to the formation of low-melting eutectics, in particular, with silica. When products based on carbonate clay are fired at temperatures above 1000°C, a vitreous phase is rapidly formed within a short temperature interval. The effect of carbonates as fluxes (even in a significant amount) is not manifested in firing under 1000°C, but the strength of the product perceptibly de-

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TABLE 1

Clay variety [2], deposit	Weight content %, in argillaceous material							
	SiO <sub>2</sub> (total)	SiO <sub>2</sub> (with- out quartz)	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O
4a, Nizhne-Suksinskoe	63.12	33.59	13.53	5.32	3.70	2.20	1.39	2.01
5a, Sakharovskoe	67.28	28.07	9.61	3.25	5.81	1.90	1.20	2.08
4b, Maksimkovskoe	33.24	24.92	11.36	3.17	24.57	1.52	0.23	2.03
70% 4a + 30% 4b	54.15	30.99	12.88	4.67	9.96	2.00	1.04	2.02
70% 5a + 30% 4b	57.07	27.13	10.14	3.22	11.44	1.79	0.91	2.07

creases. However, it is possible to obtain a ceramic material with required properties even from a mixture with a certain quantity of calcium-bearing and alkaline components even below 1000°C [3].

The formation of hercynite  $\text{FeO} \cdot \text{Al}_2\text{O}_3$ , mullite, and anorthite ( $\text{Al}_2\text{O}_3 + 2\text{SiO}_2 + \text{CaCO}_3 = \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + \text{CO}_2$ ;  $\text{CaO} + \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 = \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) in clays containing  $\text{CaCO}_3$  is more probable in reducing than in oxidizing conditions. Wollastonite may be formed as well [4]. In the case of excessive  $\text{CaCO}_3$  (calcareous ferrous clay) mullite and hercynite decompose and at a temperature above 960°C form anorthite, calcium aluminates and silicates, and braunmillerite [5].

Dolomite may cause the formation of cordierite in a ceramic material. Dehydrated clay and inorganic impurities of  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{SiO}_2$  and other oxides accelerate the reactions of decarbonization, which may be related to the increased probability of phase formation with participation of  $\text{CaO}$  and  $\text{MgO}$ . Thus, diopside  $\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$  can be formed in the presence of dolomite, whereas aluminoferrites and ferrites can be formed in the presence of  $\text{CaO}$  and  $\text{Fe}_2\text{O}_3$  [5].

Gypsum  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is also an intense flux. It becomes fused with clay as a transparent greenish glass manifested as vitreous sites [5]. Therefore, it can be assumed that gypsum contained in calcareous clays affects the sintering process.

One of the main components in numerous argillaceous minerals is  $\text{SiO}_2$ . Argillaceous minerals containing  $\text{SiO}$  decompose under heating and form reaction-active silica. It first becomes bound to the oxides of alkali metals and calcium, and in a reducing medium with  $\text{FeO}$  as well. At a temperature of 600°C,  $\text{SiO}_2$  and  $\text{CaO}$  form  $\beta\text{-Ca}_2\text{SiO}_4$ . The rate of this reaction grows significantly in the presence of iron oxides. Magnesium and aluminum oxides bind silica only at a temperature above 800°C with formation of  $\text{Mg}_2\text{SiO}_4$  and mullite  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , respectively.

Clay variety 5a contains 67.28%  $\text{SiO}_2$  (including 39.21% quartz), and variety 4a contains 63.12%  $\text{SiO}_2$  (including 29.53% quartz). Except for quartz, the quantity of silica in the first clay variety is 28.07% and in the second one 33.59%. Consequently, argillaceous minerals in clay 5a under firing will produce a smaller quantity of reaction-capable amorphous silica. The content of  $\text{SiO}_2$  except for quartz (8.32%) in calcareous clay is equal to 24.92%. Calculations

demonstrate that a mixture of 70% clay 5a and 30% lime clay contains 27.13%  $\text{SiO}_2$ , i.e., less than initial clay variety 5a. Accordingly, other terms being equal, silica cannot improve the strength properties of samples molded from this mixture with the lime clay.

The low sintering temperature is determined by an increased content of the potassium ion [5]. In this case potassium and sodium ions do not produce a strength increase, since their content is identical in both clay varieties.

The sinterability of clay to a great extent depends on  $\text{Al}_2\text{O}_3$ . The higher its content, the better is the sinterability of the argillaceous material. Clay variety 5a contains 9.61%  $\text{Al}_2\text{O}_3$ , whereas variety 4a has a significantly higher content: 13.53%. This is mainly responsible for the better strength parameters of samples made of the latter clay. The lime clay contains 11.36%  $\text{Al}_2\text{O}_3$ , i.e., more than clay variety 5a. Consequently, adding lime clay to clay 5a increases the total quantity of  $\text{Al}_2\text{O}_3$  in the clay mixture. Adding 30% calcareous clays increases the content of  $\text{Al}_2\text{O}_3$  in the mixture to 10.14%. In this case the effect of  $\text{Al}_2\text{O}_3$  on improving sinterability is unquestionable. Adding lime clay to a mixture with a higher  $\text{Al}_2\text{O}_3$  content (variety 4a) decreases its total quantity in the mixture, accordingly, the strength parameters of ceramic material are not improved.

A reducing medium has a positive effect on the quality of finished products and activates the firing process (from 800 – 850°C to the maximal temperature). This is due to the presence of ferric oxide  $\text{FeO}$  which, unlike  $\text{Fe}_2\text{O}_3$ , has a high reactivity with respect to the main clay components [1]. Under normal conditions the reduction reactions  $\text{Fe}_2\text{O}_3 \rightarrow \text{FeO}$  are possible at a temperature of 627°C. The melting point of  $\text{FeO}$  is 150 – 200°C lower than that of  $\text{Fe}_2\text{O}_3$ . The presence of  $\text{Fe}^{2+}$  in clay facilitates the formation of new phases improving the quality of construction ceramics. The iron ion has a significant effect on subsequent rearrangement of the metaphase ions into stable phases. Iron oxide up to a temperature of 1000°C does not react with clay and does not act as a flux [5]. The reduced forms of iron catalyze the decomposition of calcium carbonate. To obtain a positive effect, the quantity of iron converted to  $\text{Fe}_2\text{O}_3$  should be not less than 4% [1, 6].

It is demonstrated in [7] that the formation of the mullite-like phase with an increased content of silica under thermal treatment of clay schist is due to the presence of organic

compounds, which create a local reducing medium under firing. The presence of organic carbon in clays also contributes to developing a reducing medium [5]. Such medium is formed in firing calcareous clay due to the presence of organic material. This influences the transition of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  and facilitates earlier sintering of clay. The organogenic origin of calcite contained in calcareous clays undoubtedly affects this process, which is one of the reasons for improving strength properties of ceramics.

The weakly sintering clay of variety 5a has 3.25%  $\text{Fe}_2\text{O}_3$ , while the well-sintering variety 4a has 5.32%. Accordingly, based on this parameter, samples of clay 4a should have better sinterability, which is corroborated by experimental data. The lime clay (variety 4b) has 3.17%  $\text{Fe}_2\text{O}_3$ , i.e., adding it to clay 5a in fact does not change the quantity of  $\text{Fe}_2\text{O}_3$  in the mixture.

The performed analysis indicates that better sinterability and, respectively, higher strength parameters are seen in samples made from initial clay 4a which contains more  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ . Naturally, this conclusion extends to clay mixtures, in particular, mixtures of polymineral and lime clays.

The content of the main montmorillonite component (MC) in clay 5a is 18%; in clay 4a, 26%, and in lime clay, 26% as well. Thus, adding lime clay to clay 5a increases the strength parameters of ceramics. The effect of the introduction of lime clay into clay variety 4a on strength parameters is minimal, since in this case the quantity of the MC does not change.

The high-temperature reactions of different montmorillonites are somewhat different. Iron-rich varieties of this mineral and forms containing potassium as the exchange cation have a small quantity of new crystalline phases under increased temperatures or none at all. The soda variety has a much lower intensity of formation of high-temperature phases. Enriching the melt with  $\text{Ca}^{2+}$  ions accelerates the volume diffusion and crystallization processes. The formation of calcium aluminosilicates proceeds intensely already at a temperature of 950°C [8].

Table 2 gives the results of determining the sum of exchange cations ( $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Mg}^{2+}$ ) in the argillaceous component (montmorillonite) of the considered clays. In our case all clays contain a MC of the calcium form, and the maximum quantity of  $\text{Ca}^{2+}$  is contained in clay 4a, i.e., in the well-sintering clay.

The technological properties of clay depend on its granulometric composition. The higher the content of particles of size below 0.01 mm, the higher the plasticity and shrinkage of clay and the higher its reactivity under sintering [5]. The authors of [7] believe that one of the reasons for the formation of a steady compound of aluminum and silicon oxides with a mullite-like structure of composition  $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ , which that has good technical properties, is the fine dispersion of the components. However, the data obtained by us

TABLE 2

Clay variety	Content, * mg · equ			
	$\text{Ca}^{2+}$	$\text{K}^+$	$\text{Mg}^{2+}$	total
5a	10.48	0.52	2.47	13.47
4a	15.97	0.26	5.76	21.99
4b	11.98	1.28	4.11	17.37

\* In all clay varieties the content of  $\text{Na}^+$  is less than 0.01 mg · equ.

disagree with this conclusion. The amount of the fraction below 0.01 mm in clay 5a is 94.4%, and in clay 4a, 87.7%, i.e., its content is higher in the poorly sintering clay. The lime clay contains 85.0% of this fraction; therefore, the granulometric composition cannot be the reason for the increasing strength of ceramic samples prepared from a mixture of clays 5a and 4b.

Thus, the increase in the strength parameters of ceramics molded from poorly sintering argillaceous material and calcareous clay occurs because of the following factors:

- the increased content of the total quantity of the montmorillonite component in the batch;
- the organogenic nature of calcite in the lime clay, which contributes to the formation of a local reducing medium in firing that affects the transition of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  and facilitates earlier sintering of clay;
- the presence of a gypsum impurity, which is an intense flux, in lime clays.

## REFERENCES

1. G. L. Moisov, "The development of efficient chromophore additives for producing tinted ceramic brick at Krasnodar Region factories," *Stroit. Mater.*, No. 10, 16 – 18 (2001).
2. A. V. Kornilov and E. N. Permyakov, "Classification of clay materials based on their mineralogical-technological varieties with prediction of finished product quality," in: *Proc. Intern. Scient. Conf. "Clay and Argillaceous Minerals"* [in Russian], Voronezh (2004), pp. 71 – 73.
3. N. D. Yatsenko, N. A. Vil'bitskaya, S. P. Golovanova, et al., "Intensification of sintering of calcium-bearing ceramic mixtures," *Stroit. Mater.*, No. 9, 32 – 34 (2000).
4. S. P. Golovanova, A. P. Zubekhin, and O. V. Likhota, "Bleaching and intensification of sintering of ceramics in using iron-bearing clays," *Stroit. Mater.*, No. 12, 9 – 11 (2004).
5. A. I. Avgustinik, *Ceramics* [in Russian], Stroiizdat, Leningrad (1975).
6. N. S. Kashkaev and E. Sh. Sheinman, *Production of Clay Brick* [in Russian], Vysshaya Shkola, Moscow (1978).
7. R. V. Mkrtchyan, A. A. Shmakov, and R. A. Musaev, "Clay schist of Dzherdansko deposit as a high-quality ceramic material," *Stroit. Mater.*, No. 5, 29 – 31 (2002).
8. A. K. Abdurakhmanov, A. M. Éminov, and G. N. Maslennikova, "Stages of ceramic structure formation in the presence of additives," *Stroit. Mater.*, No. 10, 21 – 23 (2000).